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Mit Diborid beschichtete Prägefläche

Surface d'estampage revêtue de diborure

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(56) References cited:  
**EP-A- 0 674 020 DE-A- 2 141 928**

- **BRANDSTETTER E ET AL: "A TRANSMISSION ELECTRON MICROSCOPY STUDY ON SPUTTERED ZR-B AND ZR-B-N FILMS" THIN SOLID FILMS, vol. 201, no. 1, 5 June 1991, pages 123-135, XP000261648**

- **RIVIERE J P ET AL: "CRYSTALLINE TiB2 COATINGS PREPARED BY ION-BEAM-ASSISTED DEPOSITION" THIN SOLID FILMS, vol. 204, no. 1, 20 September 1991, pages 151-161, XP000275037**
- **DENG H ET AL: "Growth, structure and stress of dc magnetron sputtered TiB/sub 2/ thin films" THIN FILMS: STRESSES AND MECHANICAL PROPERTIES V. SYMPOSIUM, THIN FILMS: STRESSES AND MECHANICAL PROPERTIES V. SYMPOSIUM, BOSTON, MA, USA, 28 NOV.-2 DEC. 1994, 1995, PITTSBURGH, PA, USA, MATER. RES. SOC, USA, pages 181-186, XP002049332**
- **MITTERER C ET AL: "Sputter deposition of wear-resistant coatings within the system Zr-B-N" SECOND INTERNATIONAL CONFERENCE ON PLASMA SURFACE ENGINEERING, GARMISCH-PARTENKIRCHEN, WEST GERMANY, 10-14 SEPT. 1990, vol. A140, ISSN 0921-5093, MATERIALS SCIENCE & ENGINEERING A (STRUCTURAL MATERIALS: PROPERTIES, MICROSTRUCTURE AND PROCESSING), 7 JULY 1991, SWITZERLAND, pages 670-675, XP002049333**
- **LARSSON T ET AL: "REACTIVE SPUTTERING OF TITANIUM BORIDE" THIN SOLID FILMS, vol. 172, no. 1, 1 May 1989, pages 133-140, XP000052937**

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## Description

BACKGROUND OF THE INVENTION5 1. Field of the Invention

[0001] This invention relates to coated, abrasion resistant press plates used in making abrasion resistant decorative laminate, to the coating of press plates and to the making of laminate with these press plates. Grit, e.g., alumina particles, on the pressing surface of abrasion resistant decorative laminate can scratch press plates and reduce the visual quality of laminate thereafter made with the press plate. Press plates of this invention are particularly useful in making abrasion resistant high gloss decorative laminate.

2. Description of the Related Art

15 [0002] In the manufacture of decorative laminate, layers of resin impregnated paper are pressed against press plates under conditions of temperature and pressure to cure the resin and bond the layers together. A high gloss press plate imparts a high gloss surface to laminate. A textured surface imparts a textured surface to laminate. These press plates are extremely uniform, with even microscopic discontinuities being minimized. The quality of a high gloss polished press plate can be determined by viewing reflected images on its surface and scrutinizing the reflected images for optical discrepancies. Grit on the surface of laminate causes micro scratching of stainless steel press plates normally used in the manufacture of decorative laminate thus destroying the micro finish of the press plate. Press plates can also be scratched by press plate handling equipment and by debris from pressing equipment or materials used in making laminate. (Laurence U.S. Patent 5,244,375)

20 [0003] Melamine resin coated decorative laminate is pressed at temperatures of about 230-310°F (110-155°C) and pressures of about 300-2000 psi 2.05-13.78 MPa and preferably about 750-1500 psi 5.17-10.34 MPa. Heating to these temperatures and cooling to room temperature results in substantial expansion and contraction of the laminate and of the press plate. Expansion and contraction of the laminate and press plate will not be the same, resulting in tile movement of grit on the pressing surface of laminate across the press plate.

30 [0004] It is disclosed in National Electrical Manufacturers Association (NEMA. Standards Publication No. LD 3. that gloss finish laminate has a gloss of 70-100+ High gloss textured finish laminate is disclosed as having a gloss of 21-40. Black glass with a gloss of 94±1 measured at an angle of 60 degrees, is disclosed as the NEMA Standard 3.2.2 for calibrating a gloss meter for 60 degree angle gloss measurements.

[0005] Even discontinuities in high gloss press plates that can only be seen with a microscope can impart visible surface defects to a high gloss surface of laminate. Any scratching of high gloss press plates imparts visible surface defects to high gloss surfaces of laminate and reduce gloss level.

35 [0006] Grit on the decorative surface of laminate imparts abrasion resistance, a commercially desirable characteristic of laminate. Particles of alumina are commonly used as grit in making decorative laminate. The Vickers hardness of alumina is disclosed in "Tribology: Friction and wear of Engineering Materials", I. M. Hutchings, CRC Press 1992, to be 1800 to 2000. A useful range of particle sizes is about 10 to about 75 microns. Grit of about 25-60 µm (microns) is preferred. Optimum abrasion resistance is obtained in the particle size range of about 40 µm to 60 µm (40 to 60 microns) (Lane et. al. U.S. Patent 3,798,111)

40 [0007] Alumina having a maximum particle size of 9 microns is disclosed as being effective for imparting a wear resistant surface to glossy decorative laminate. Wear resistance is defined as the resistance of a glossy laminate to loss of gloss when the surface of laminate is exposed to the abrasive effects of sliding objects. It is acknowledged that the resulting laminate does not meet NEMA LD 3.13 requirements to be considered as abrasion resistant. However, it is disclosed that glossy press plates are not scratched substantially if the grit particle size is maintained at less than 9 µm (9 microns). Lex et al. U.S. Patent 4,971,855)

45 [0008] The use of a 410 stainless steel press plate hardened by nitriding is disclosed for making high gloss decorative laminate. After pressing 100 sheets of high gloss laminate with 6 µm (6 micron) and 15 µm (15 micron) grit, the gloss of the pressed laminate remained good to very good. The nitrided press plate exposed to the 6 micron grit was rebuffed after 234 cycles and produced acceptable laminate quality for at least another 103 cycles. Nitrided press plates exposed to 30 micron grit offered limited durability. It is disclosed that the 410 stainless steel press plate used for nitriding had a Rockwell, "C" scale hardness of 38-45 and that the nitrided surface had a Rockwell, "C" scale hardness of 60-70. The equivalent Vickers hardness of 410 stainless steel is about 370-440, based on a conversion table published in "Metals Handbook. Mechanical Testing", Vol. 8, 9th ed., ASM, 1985. The equivalent Vickers hardness of nitrided 410 stainless steel is about 500-1000, based on a conversion table published in "Metals Handbook, Mechanical Testing", Vol. 8, 9th ed., ASM, 1985. (Laurence U.S. Patent 5,244,375)

55 [0009] Laminate with 35 µm (35 micron) average particle size alumina at its surface (PGA 822 overlay available

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commercially from Mead Corporation) has been pressed with high gloss press plates coated with titanium nitride. After ten pressings, the titanium nitride coated press plates had about 15 scratches per square centimeter. A control 410 stainless steel press plate had about 500 scratches per square centimeter. The Vickers hardness of titanium nitride is disclosed in "Tribology: Friction and wear of Engineering Materials", M. Hutchings, CRC Press, 1992, to be 1200 to 2000.

**[0010]** The control press plate and the press plate on which the titanium nitride was coated were cut from the same stainless steel pressing plate. The scratches was visible under a light microscope at 40X magnification. Titanium nitride was coated onto 410 stainless steel high gloss press plates in a magnetron sputter coating system. The use of a magnetron sputter coating system for applying a titanium nitride coating is disclosed in "Multi-Cathode Unbalanced Magnetron Sputtering Systems," Sproul. Surface and coating Technology, 49 (1991). The use of a magnetron sputter coating system for cleaning the surface that is to be coated is disclosed in "A New Sputter Cleaning System For Metallic Substrates," Schiller et. al., Thin Solid Films. 33 (1976)

**[0011]** Additionally, the color of the laminate pressed with the titanium nitride coated press plate was different than the color of the laminate pressed with the control press plate. An ASTM D 2244 color difference in comparison to a standard of less than ( $\pm 0.5$ )  $\Delta E$  is considered as an acceptable color match to the standard. The ASTM D 2244 color difference between a standard and laminate pressed with the titanium nitride coated press plate was greater than (0.5)  $\Delta E$ . The titanium nitride coated press plate and laminate pressed therefrom had a bronze appearance. The control press plate and the laminate pressed therefrom did not have a bronze appearance. Laminate pressed with the control press plate had an STM D 2244 color difference when compared with the standard of less than (0.5)  $\Delta E$ .

**[0012]** Iron based cutting tools have been sputter coated with 2-6  $\mu m$  (microns) of titanium diboride. The sputtering is carried out in an argon or krypton beam of ions accelerated to 1300-1800 volts as a broad-beam ion source. A titanium diboride target is arranged as a cathode. The tool is heated to about 200°C (392°F). Sputtering is done under a vacuum of about 4-6 milli-Torr. Titanium diboride has an extremely high Vickers micro-hardness value, typically about 3600, which is not only considerably higher than other borides but also substantially higher than other carbides or nitrides. Titanium diboride is also particularly noted for its high density, e.g. 88% of theoretical density, a low resistivity of 30 micro-ohms centimeters, a high strength of about  $2,758 \times 10^9 N/M^2$  (40,000 psi.) and a coefficient of thermal expansion which is about  $8.1 \times 10^{-6}$  at the temperature range of 20°-800°C (68-1472°F). (Moskowitz et al., U.S. Patent Number 4,820,392).

**[0013]** Control conditions for sputter coating are disclosed in "Influence of Apparatus Geometry and Deposition Conditions on the structure and Topography of Thick Sputtered Coatings" Thornton, Journal of Vacuum Science Technology, Volume 11, Number 4 (July/August 1974) and "Sputtering" Thornton et al., Metals Handbook, Ninth Edition American Society for Metals, Metals Park, Ohio 44073, Volume 5, pp 412-416, (1982).

**[0014]** DE-A-214192 discloses the manufacture of a pressing tool for form-pressing of highly abrasive plastics, in which a hardened chromium steel plate is coated with borides of Ti, Zr, Hf, V, Cr, Ta, Mo and W, particularly TiB<sub>2</sub>. Those coatings have Vickers microhardnesses of 19.6 to 39.2 MN/m<sup>2</sup> (2000-4000 kp/mm<sup>2</sup>). The polished steel plate is heated to 800°C in a reaction tube (purged with hydrogen gas) and subsequently coated with a conventional CVD process.

**[0015]** MITTER C. ET EL : "Sputter deposition of wear-resistant coatings within the system Zr-B-2-N" SECOND INTERNATIONAL CONFERENCE ON PLASMA SURFACE ENGINEERING, GARMISCH-PARTENKIRCHEN (DE) 10-14 Sept. 1990, vol. A140, ISSN 0921-5093, MATERIALS SCIENCE & ENGINEERING A (STRUCTURAL MATERIALS : PROPERTIES, MICRO-STRUCTURE AND PROCESSING), 7 July 1991, pages 670-675 discloses the production of wear-resistant zirconium boride coatings on steel substrates by non-reactive magnetron sputtering. The resulting coatings have a Vickers microhardness up to 2300HV 0.02.

**[0016]** There is a need for a hard coating on a press plates, continuous belt and other pressing surfaces that imparts a color to laminate having an ASTM D 2244 color difference in comparison to a standard of less than ( $\pm 5$ )  $\Delta E$ . There is a need for a coating that can be applied to a pressing surface without changing the appearance of the finish on the pressing surface. There is a need for a pressing surface that is not scratched when used in pressing laminate coated with alumina particles of greater than 10 $\mu m$  and preferably greater than 25 $\mu m$ . There is a particular need for a pressing surface that is not scratched when used in pressing high gloss laminate with an ASTM 2457 60 degree angle gloss of greater than 70, when the surface of the laminate is coated with 25-60 $\mu m$  alumina particles.

**[0017]** According to the present invention, there is provided a method of manufacturing a press plate with a smooth high-gloss, wear resistant surface, the method comprising providing a metal press plate with a smooth, high-gloss, clean surface, and coating said surface with a diboride in a magnetron sputtering coating system, said diboride being a diboride of hafnium, molybdenum, tantalum, titanium, tungsten, vanadium or zirconium, the diboride coating having a Vickers hardness of at least 2000.

**[0018]** The color, gloss and surface appearance of laminate made with such a press plate are substantially the same as the color and gloss of laminate made with the metal plate before the coating is applied. The preferred diborides for coating laminate pressing surfaces are titanium diboride or zirconium diboride. The most preferred diboride for coating laminate pressing surfaces is titanium diboride. It is believed that titanium diboride is more commonly used commercially

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for coating surfaces than other members of the diborides of this invention because it can be sputter coated in a magnetron sputtering system at a higher deposition rate.

[0019] The Vickers hardness of at least 2000 of the diboride coating of a press plate according to the invention allows for press plates to be used for pressing laminate with 25-60 micron or larger alumina particles at the pressing surface of the laminate without being scratched. A coating of about 3 microns has sufficient hardness to resist scratching by alumina particles on the pressing surface of laminate. The hardness of the coating can be controlled in a planar magnetron sputter coating system by those skilled in the use of these systems.

[0020] It has been discovered that the diboride coating can be coated on a pressing surface with sufficient bond strength for use in pressing high pressure laminate.

[0021] A minimum bond strength of 1.6 and preferably 1.8 kilogram force (kgf) (15.7N and preferably 20.8N) determined by diamond scratching bond testing is believed sufficient. Diboride coatings of greater than 6 $\mu$ m (6 microns) can have lower bond strengths due to stresses produced during coating.

[0022] In preferred embodiments of this invention, bonding to the pressing surface is enhanced by thoroughly cleaning the pressing surface before introducing the pressing surface into a magnetron sputter coating system. Bonding is further enhanced by etching the pressing surface with the magnetron sputter coating system prior to applying the titanium boride coating. Cleaning, anodic etching, cathodic etching and etching with radio frequency (RF) can be accomplished by methods known to those skilled in the use of a magnetron sputter coating system. It has been discovered that a layer of titanium applied directly onto the pressing surface before applying the diboride coating of this invention further enhances the bonding of the diboride. Improving bonding by cleaning, etching and the use of an intermediate layer between the coating and substrate are known to those skilled in the art of using magnetron sputter coating systems.

#### DETAILED DESCRIPTION OF THE INVENTION

[0023] Black, high gloss, high pressure laminate was pressed with titanium diboride coated press plates shown on Table 1. These press plates had been finished for imparting an ASTM D 2457 60 degree angle gloss of about 100 to laminate before being coated with titanium diboride. The ASTM D 2244 color difference between a standard and laminate pressed with the titanium diboride coated press plates shown on Table 1 was less than (0.5)  $\Delta E$ . Gloss and color differences on Table 1, are averages of measurements made on 10 laminates.

Table 1

Press Plate	Gloss and Color Differences	
	ASTM Gloss @ 60°	ASTM Color Difference, $\Delta E$
3000-1	101	0.20
3000-2	100	0.25
6000-1	101	0.35
6000-2	103	0.40
6000-3	102	0.30
6000-4	102	0.40
6000-5	103	0.45
6000-6	101	0.45

[0024] Additionally, high gloss Press Plate 3000-2 and a control press plate have been used in the pressing of 760 sheets of high pressure, black, high gloss laminate with 35  $\mu$ m (35 micron) average particle size alumina particles on its pressing surface. Laminate was pressed with these press plates at about 1000 psi (6.89 MPa) and 280°F (138°C). The pressing surface of the laminate is commercially available overlay sheet with 35  $\mu$ m (35 micron) alumina grit (PGA 822 from Mead). Press Plate 3000-2 and the control press plate were cut from a high gloss, 410 stainless steel press plate that had been finished for imparting an ASTM D 2457 60 degree angle gloss of about 100 to laminate. Press Plate 3000-2 and the control press plate measure about twelve inches along one side and eleven inches along their other side. Press Plate 3000-2 was coated with about 5  $\mu$ m (five microns) of titanium diboride in a magnetron sputter coating system. The titanium diboride coating was applied in 17 scans, applying about 0.3  $\mu$ m (3000 angstroms) of titanium diboride per scan. The other was used as a control.

[0025] The first sheet of black, high gloss laminate with 35  $\mu$ m (35 micron) average particle size alumina particles on its pressing surface pressed with the control press plate had an ASTM D 2244 color difference in comparison to a standard of about (0.25)  $\Delta E$ . The first sheet of black, high gloss laminate pressed with Press Plate 3000-2 had an ASTM D 2244 color difference in comparison to a standard of about (0.15)  $\Delta E$ .

[0026] The first sheet of black laminate pressed with the control press plate had an ASTM D 2457 60 degree angle

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gloss of about 100 to laminate. The 760th sheet of black laminate pressed with the control press plate had an ASTM D 2457, 60 degree angle gloss of less than 70. The control press plate imparted a 60 degree angle gloss of less than 90 to black laminate after it had pressed about 160 sheets. It is believed that laminate with a 60 degree angle gloss of less than 90 is not commercially acceptable as a high gloss laminate.

5 [0027] These 760 sheets of black laminate pressed with Press Plate 3000-2 had an ASTM D 2457 60 degree angle gloss of about 100. Press Plate 3000-2 has been viewed under a microscope for scratches after pressing these 760 sheets of black laminate and none have been found. The control press plate is heavily scratched.

[0028] No differences were observed in the surface appearance of laminate pressed with the Press Plates shown on Table 1 and control press plates.

10 [0029] Titanium diboride was coated onto the high gloss press plate in a magnetron sputter coating system under a number of conditions. It is also believed that a coating of at least 3  $\mu\text{m}$  (3 microns) is necessary for achieving a Vickers hardness of at least 2000 and that adhesion decreases at coating thicknesses of 6  $\mu\text{m}$  (6 microns) or greater. Hardness and adhesion can be controlled, as known to those skilled in the art, by the pressure and temperature under which press plates are coated with the diborides of this invention and the power (amperes and volts) used in coating the diborides of this invention on press plates.

15 [0030] A textured press plate coated with titanium diboride, hereinafter "Press Plate 3000-3" and a control press plate been used in the pressing of greater than 450 sheets of high pressure black, textured laminate with 35  $\mu\text{m}$  (35 micron) average particle size alumina particles on its pressing surface. This laminate was pressed at about 1000 psi (6.89 MPa) and 280°F (138°C). Press Plate 3000-3 and the control press plate were cut from a textured, 630 stainless steel press plate that had been finished for imparting an ASTM D 2457 60 degree angle gloss of about 10 to laminate. Press Plate 3000-3 and the control press plate measure about 29.4 cm (twelve inches) along each side. Press Plate 3000-3 was coated with about 6  $\mu\text{m}$  (six microns) of titanium diboride in a magnetron sputter coating system. The titanium diboride coating was applied in 20 scans, applying about 0.3  $\mu\text{m}$  (3000 angstroms) of titanium diboride per scan.

20 [0031] The first sheet of this black, textured laminate pressed with the control press plate had an ASTM D 2244 color difference in comparison to a standard of about (0.22)  $\Delta E$ . Black, high gloss laminate pressed with Press Plate 3000-3 had an ASTM D 2244 color difference in comparison to a standard of about (0.08)  $\Delta E$ .

25 [0032] The first sheet of this black laminate pressed with the control press plate had an ASTM D 2457, 60 degree angle gloss of about 9.5. The 450th sheet of this black laminate pressed with the control press plate had an ASTM D 2457, 60 degree angle gloss of about 8. This black laminate pressed with Press Plate 3000-3 had an ASTM D 2457 60 degree angle gloss of about 10.

30 [0033] No differences were observed in the surface appearance of laminate pressed with the Press Plate 3000-3 and a control press plate.

[0034] The press plates on Table 1 and Press Plate 3000-3 were cleaned and then etched under radio frequency conditions in a planar magnetron sputter coating system. These press plates were then coated with titanium diboride in the magnetron sputter coating system under the following averaged conditions.

#### Cleaning

40 [0035]

- chemical cleaning      wipe with ethanol, trichloroethane and acetone
- physical cleaning      5 minute nitrogen gas blow over press plate

#### Radio Frequency Etching Conditions

45

[0036]

- gas medium      argon
- in./ minute (cm / minute) scan speed      1(2.54)
- 50 • mTorr (mPa)      10 (1.3)
- mA/sq. in. (mA/sq. cm.)      3.5(54)
- kV      75

#### Titanium Diboride Coating Conditions

55

[0037]

- gas medium      argon

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- in./ minute (cm./ minute) scan speed 1(2.54)
- mTorr 7 (0.9)
- mA/sq. in. (mA/sq. cm.) 83(13)
- kV .3

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Coating Conditions and Properties**[0038]**

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Press Plate	Scan Rate Å/scan	Scans	Thickness microns	Adhesion kgf	Hardness HV
3000-1	3000	14	4.2	1.7	2280
3000-2	3000	17	5.1	2.1	2830
3000-3	3000	20	5.5	2.0	2700
6000-1	6000	6	3.7	1.8	1940
6000-2	6000	6	3.7	1.8	2160
6000-3	6000	7	4.4	1.8	2250
6000-4	6000	7	4.3	2.0	2190
6000-5	6000	10	6	2.2	2880
6000-6	6000	10	6	2.0	2850
1 µm (1 micron) = 10,000 Å units					

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**[0039]** Three high gloss press plates, measuring about 1.22m by 2.44m (four feet by eight feet) were made. These press plates are referred to as Press Plates 3-1 3-2, and 3-3 These press plates were sputter coated with titanium diboride under planar magnetron discharge conditions.

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**[0040]** Press Plates 3-1, 3-1, and 3-3 were anodically etched and then coated with titanium and titanium diboride in a planar magnetron sputter coating system under the following averaged conditions. These press plates were chemically cleaned before they were placed into the sputter coating system. The temperature of these press plates during etching and coating was about 300°F(149°C) These press plates did not warp at this temperature

35

Cleaning (Press Plates 3-1, 3-2, and 3-3)				
· chemical cleaning wipe with ethanol, trichloroethane and acetone				
Anodic Etching Conditions (Press Plates		3-1,	3-2,	3-3)
· gas medium		argon	argon	argon
· in./ minute (cm./ minute) scan speed		3(7.6)	3(7.6)	3(7.6)
· mTorr (mPa)		25 (3.25)	24 (3.12)	10 (1.3)
· mA/sq. in. (mA/sq. cm.)		4.6(.72)	2.9(.45)	2.9(45)
· kV		24	.23	.24
· number of scans		1	1	5
Titanium Coating Conditions (Press Plates		3-1	3-2,	3-3)
· gas medium		argon	argon	argon
· in./ minute (cm./ minute) scan speed		3(7.6)	3(7.6)	3(7.6)
· mTorr		1.6 (0.2)	1.2 (0.16)	2.7 (0.35)
· mA/sq. in. (mA/sq. cm.)		70(11)	70(11)	70(11)
· kV		.52	.52	.43
· number of Ti scans		1	1	1
Titanium Diboride Coating Conditions (Press Plates		3-1,	3-2,	3-3)
· gas medium		argon	argon	argon
· in./ minute (cm./minute) scan speed		3(7.6)	3(7.6)	3(7.6)
· mTorr		1.6 (0.2)	1.2 (0.16)	2.7 (0.35)
· mA/sq. in. (mA/sq. cm.)		71(11)	75(12)	70(11)

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(continued)

5	• kV	.52	.60	.50
	• number of TiB <sub>2</sub> scans	8	12	18
	• deposition rate (Å/scan) ( $m \times 10^{-10}$ )	4125	5500	3000
10	Properties of TiB <sub>2</sub> /Ti Coating (Press Plates)	3-1	3-2	3-3)
	• thickness (microns) ( $\mu m$ )	3 3	6.6	5.4
	• adhesion (kgf) (N)	*	1.2*(11-8)	**
	• hardness HV (N $\times$ 9.81)	2000	2500	**

\* TiB<sub>2</sub>/Ti coating separated from Press Plates 3-1 and 3-2 during the pressing of laminate.

\*\* The hardness and adhesion of Press Plate 3-3 has not been measured Hardness and adhesion testing destroys the surface of a press plate.

15 [0041] Press Plate 3-3 has been used in the pressing of greater than 1200 sheets of high pressure, black, high gloss laminate with 35  $\mu m$  (35 micron) average particle size alumina particles on their pressing surfaces. Press Plates 3-3 was viewed for scratches after pressing these 1200 sheets of laminate and none have been found The titanium diboride coating on Press Plates 3-1 and 3-2, separated from the stainless steel substrate after pressing less than 100 sheets of laminate.

20 [0042] A zirconium diboride coated high gloss press plate of this invention and a control press plate have each been used in the pressing of 10 sheets of black, high gloss laminate This laminate had an ASTM D 2244 color difference in comparison to a standard of about (0.26)  $\Delta E$  and an ASTM D 2457, 60 degree angle gloss of about 100. No differences were observed in the surface appearance of laminate pressed with the zirconium coated and control press plates.

25 [0043] A zirconium diboride coated high gloss press plate of this invention has been used in the pressing of 10 sheets of black, high gloss laminate with 35  $\mu m$  (35 micron) average particle size alumina particles on its pressing surface. This laminate was pressed at about 1000 psi (6.89 MPa) and 280°F (138°C). A commercially available overlay sheet with 35 micron alumina grit (PGA 822 from Mead) is the pressing surface of the laminate. No scratches were observed on this press plate after the pressing of these 10 sheets of laminate.

30 [0044] This zirconium diboride press plate was cut from a high gloss, 410 stainless steel press plate having an ASTM D 2457, that had been finished for imparting a 60 degree angle gloss of about 100 to laminate. Two press plates measuring about twelve inches along each side were cut from this press plate. One was coated with about five microns of zirconium diboride in a planar magnetron sputter coating system. This press plate was etched under radio frequency conditions for about 15 minutes before the titanium diboride coating was applied. A 6 micron zirconium diboride coating was applied in 15 scans, applying about 4,000 angstroms (0.4  $\mu m$ ) of zirconium diboride per scan in a planar magnetron sputter coating system under the following averaged conditions.

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Cleaning

## [0045]

- 40
- chemical cleaning wipe with ethanol, trichloroethane and acetone
  - physical cleaning 5 minute nitrogen gas blow over press plate

Radio Frequency Etching Conditions

45

## [0046]

- 50
- gas medium argon
  - in./ minute (cm./ minute) scan speed 1(2.54)
  - mTorr 10
  - mA/sq. in. (mA/sq. cm) 3.5( .54)
  - kV .75

Zirconium Diboride Coating Conditions

55

## [0047]

- gas medium argon

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- in./ minute (cm./ minute) scan speed 1(2.54)
- mTorr 7
- mA/sq. in. (mA/sq. cm.) 56(9)
- kV .4

**[0048]** Black, laminate has been pressed with press plates, measuring six inches by six inches (15.24 cm X 15.24 cm), coated with titanium nitride in a magnetron sputter coating system. The test results shown on Table 3 are the average results of pressing five sheets of laminate with each press plate.

Table 3

Laminate Pressed With Titanium Nitride Coated Press Plates				
	control #8	TiN #8	control #9	TiN #9
ASTM Gloss @ 60°	100	95	100	95
ASTM Color Difference. ΔE	0.30	0.75	0.35	0.90

**[0049]** The gloss of the laminate pressed with the titanium nitride coated press plate was lower than the gloss of laminate pressed with the control press plate. The color of the laminate pressed with the titanium nitride coated press plate was significantly different from the color of the laminate pressed with the uncoated control press plate. The titanium nitride coated press plates and laminate pressed with the titanium nitride press plates had a bronze appearance.

**[0050]** Black, laminate has been pressed with press plates, measuring six inches by six inches (15.24 cm X 15.24 cm), coated with niobium nitride in a magnetron sputter coating system. The test results shown on Table 4 are the average results of pressing five sheets of laminate with each press plate.

Table 4

Laminate Pressed With Niobium Nitride Coated Press Plates			
Black, High Gloss Laminate	control	B3 (3μm)	B5 (5μm)
ASTM Gloss @ 60°	106	102	101
ASTM Color Difference. ΔE	0.09	0.65	0.85

**[0051]** The gloss of laminate pressed with niobium nitride coated press plates was lower than the gloss of laminate pressed with the press plate before it was coated. The color of laminate pressed with the niobium nitride coated press plates was significantly different from laminate pressed with press plates before they were coated.

**[0052]** Black, laminate has been pressed with press plates, measuring six inches by six inches (15.24 cm X 15.24 cm), coated with diamond like coating in a magnetron sputter coating system. The laminate stuck to the diamond like coated press plate and was destroyed when it was separated.

## Claims

1. A method of manufacturing a press plate with a smooth high-gloss, wear resistant surface, the method comprising providing a metal press plate with a smooth, high-gloss, clean surface, and coating said surface with a diboride in a magnetron sputtering coating system, said diboride being a diboride of hafnium, molybdenum, tantalum, titanium, tungsten, vanadium or zirconium, the diboride coating having a Vickers hardness of at least 2000.
2. A method according to claim 1 wherein said diboride is titanium diboride.
3. A method according to claim 1 wherein said diboride is zirconium diboride.
4. A method according to claim 2 wherein the step of providing said metal press plate comprises the step of providing a steel plate with a smooth, high-gloss, clean surface, coating said surface with a layer of titanium in a magnetron sputtering coating system and subsequently applying said diboride coating to the surface of said titanium layer in a magnetron sputtering coating system.
5. A method according to any of claims 1 to 4 wherein said diboride is applied to said surface to a total thickness of 3μm to 6μm.

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6. A method according to claim 5 wherein said diboride coating is applied in a plurality of scans, so as to apply a boride thickness of 0.3 to 0.55  $\mu\text{m}$  (3000 to 5500 Å) per scan, up to said total thickness of 3  $\mu\text{m}$  to 6  $\mu\text{m}$ .
7. A method according to any preceding claim wherein said metal press plate with said smooth high-gloss clean surface is provided by finishing a stainless steel plate to a high gloss finish, chemically cleaning the finished surface, placing the plate in a magnetron sputter coating system and anodically etching the finished surface, and thereafter coating the anodically etched surface with a layer of titanium in the magnetron sputtering system and subsequently applying said diboride coating to the surface of the titanium layer by magnetron sputtering.

## Patentansprüche

1. Verfahren zur Herstellung einer Preßplatte mit einer glatten hochglänzenden, abriebfesten Oberfläche, wobei das Verfahren das Bereitstellen einer Metallpreßplatte mit einer glatten, hochglänzenden, sauberen Oberfläche und das Beschichten besagter Oberfläche mit einem Diborid in einem Magnetron-Sputter-Beschichtungssystem umfaßt, wobei besagtes Diborid ein Diborid von Hafnium, Molybdän, Tantal, Titan, Wolfram, Vanadium oder Zirkonium ist, wobei die Diborid-Beschichtung eine Vickers-Härte von wenigstens 2000 aufweist.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** besagtes Diborid Titandiborid ist.
3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** besagtes Diborid Zirkonumdiborid ist.
4. Verfahren nach Anspruch 2, **dadurch gekennzeichnet, daß** der Schritt des Bereitstellens besagter Metallpreßplatte den Schritt des Bereitstellens einer Stahlplatte mit einer glatten, hochglänzenden, sauberen Oberfläche, des Beschichtens besagter Oberfläche mit einer Schicht aus Titan in einem Magnetron-Sputter-Beschichtungssystem und des anschließenden Aufbringens besagter Diborid-Beschichtung auf die Oberfläche besagter Titanschicht in einem Magnetron-Sputter-Beschichtungssystem umfaßt.
5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, daß** besagtes Diborid auf besagte Oberfläche bis zu einer Gesamtdicke von 3  $\mu\text{m}$  bis 6  $\mu\text{m}$  aufgebracht wird.
6. Verfahren nach Anspruch 5, **dadurch gekennzeichnet, daß** besagte Diborid-Beschichtung in einer Mehrzahl von Scans aufgebracht wird, um eine Borid-Dicke von 0,3 bis 0,55  $\mu\text{m}$  (3000 bis 5500 Å) pro Scan aufzubringen, bis zu besagter Gesamtdicke von 3  $\mu\text{m}$  bis 6  $\mu\text{m}$ .
7. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, daß** besagte Metallpreßplatte mit besagter glatten, hochglänzenden, sauberen Oberfläche bereitgestellt wird durch Finishbearbeitung einer rostfreien Stahlplatte zu einem hochglänzenden Finish, chemische Reinigung der finishbearbeiteten Oberfläche, Einbringen der Platte in ein Magnetron-Sputter-Beschichtungssystem und anodisches Ätzen der finishbearbeiteten Oberfläche und danach Beschichten der anodisch geätzten Oberfläche mit einer Titanschicht im Magnetron-Sputter-System und anschließend Aufbringen besagter Diborid-Beschichtung auf die Oberfläche der Titanschicht durch Magnetron-Sputtern.

## Revendications

1. Un procédé de fabrication d'une plaque de presse ayant une surface résistant à l'usure, à brillant élevé uniforme, le procédé consistant à prévoir une plaque de presse en métal avec une surface propre, à brillant élevé, uniforme, et à revêtir ladite surface avec un diborure dans un système de revêtement par projection de magnétron, ledit diborure étant un diborure d'hafnium, de molybdène, de tantale, de titane, de tungstène, de vanadium ou de zirconium, le revêtement de diborure ayant une dureté Vickers d'au moins 2000.
2. Un procédé selon la revendication 1, dans lequel ledit diborure est le diborure de titane.
3. Un procédé selon la revendication 1, dans lequel ledit diborure est le diborure de zirconium.
4. Un procédé selon la revendication 2, dans lequel l'étape consistant à prévoir ladite plaque de presse en métal comprend l'étape de fournir une plaque en acier avec une surface propre, à brillant élevé uniforme, à revêtir ladite

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surface avec une couche de titane dans un système de revêtement par projection de magnétron et à appliquer subséquemment ledit revêtement de diborure à la surface de ladite couche de titane dans un système de revêtement par projection de magnétron.

- 5 5. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit diborure est appliqué à ladite surface selon une épaisseur totale de 3  $\mu\text{m}$  à 6  $\mu\text{m}$ .
- 10 6. Un procédé selon la revendication 5, dans lequel ledit revêtement de diborure est appliqué selon une pluralité de balayages, de façon à appliquer une épaisseur de borure de 0,3 à 0,55  $\mu\text{m}$  (3000 à 5500 Å) par balayage, jusqu'à ladite épaisseur totale de 3  $\mu\text{m}$  à 6  $\mu\text{m}$ .
- 15 7. Un procédé selon l'une quelconque des revendications précédentes, dans lequel ladite plaque de presse en métal avec ladite surface propre à brillant élevé uniforme est obtenue par finissage d'une plaque en acier inoxydable à fini de brillant élevé, nettoyage chimique de la surface finie, mise en place de la plaque dans un système de revêtement par projection de magnétron et gravure anodique de la surface finie, et subséquemment revêtement de la surface gravée anodiquement avec une couche de titane dans le système de projection de magnétron et application subséquente dudit revêtement de diborure à la surface de la couche de titane par projection de magnétron.

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